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<b>(21) International Application Number:</b> PCT/US98/09149 <b>(22) International Filing Date:</b> 8 May 1998 (08.05.98)  <b>(30) Priority Data:</b> 60/046,118           9 May 1997 (09.05.97)           US 09/065,916        24 April 1998 (24.04.98)       US  <b>(71) Applicant:</b> THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).  <b>(72) Inventors:</b> NUNES, Raul, Victorino; 173 Shoemaker Drive, Loveland, OH 45140 (US). EVERS-SMITH, Linda; 20051 Black Oak Road, Fayetteville, OH 45118 (US). BOAT- MAN, Donn, Nathan; 7536 Carole Lane, Florence, KT 41042 (US). KRAUS, Christopher, Scott; 8907 Yorkridge Road, Guilford, IN 47022 (US).  <b>(74) Agents:</b> REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>
<b>(54) Title:</b> PIGMENTED ADHESIVE COMPOSITION FOR LAMINATING TISSUE PAPER PRODUCTS AND METHODS FOR PRODUCING SUCH COMPOSITIONS  <b>(57) Abstract</b>  An adhesive composition that is suitable for laminating absorbent paper products and paper products laminated using the adhesive composition are disclosed. The adhesive composition provides wet bond strength and a visual signal that desirable properties are maintained when the absorbent paper product becomes wet. The adhesive composition includes a water soluble or dispersible dry strength binder, a water soluble cationic wet strength resin, and a pigment. Also disclosed is a method of producing the adhesive composition. The method includes as an essential step, providing energizing means that can transfer at least about 5 watts per kilogram of power to a resin solution or dispersion as a pigment dispersion is added.		

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## PIGMENTED ADHESIVE COMPOSITION FOR LAMINATING TISSUE PAPER PRODUCTS AND METHODS FOR PRODUCING SUCH COMPOSITIONS

### FIELD OF THE INVENTION

The present invention relates to adhesive compositions for laminating multi-ply cellulosic fibrous structures such as tissue paper products, to methods for producing such adhesive compositions, and tissue products laminated using such adhesive compositions.

### BACKGROUND OF THE INVENTION

Paper products are well known in everyday life. Certain types of paper products are referred to as tissue, and are used for paper toweling, facial tissue, and bath tissue.

Tissue paper products may comprise a single ply, but frequently comprise two or more plies. As used herein, a "ply" refers to a single sheet taken off a forming wire, or the equivalent thereof, and dried without additional fibers being added thereto.

Of course, a ply may be layered with different types of fibers in each layer. Layering provides the benefits that a central layer may comprise relatively strong fibers to impart strength to the tissue paper product. Outboard of the central layer may be shorter fibers which impart a soft tactile sensation to the user. Layering may be advantageously accomplished by commonly assigned U.S. Patent 3,994,771, issued November 30, 1976 to Morgan, Jr. et al., which patent is incorporated herein by reference.

Frequently, two or more plies are joined together to make a paper product. Joining multiple plies together provides the advantage that the resulting laminate has a lower bending modulus than a single ply of equivalent thickness. This provides the benefit that, again, a softer tactile sensation is perceived by the user. Absorbency and caliper are typically improved as well. Furthermore, joining three plies together allows the

paper product to have different central and outboard plies in the laminate, to provide strength and softness respectively.

Multi-ply tissue products are typically cellulosic. As used herein, "cellulosic" refers to a paper product comprising at least about fifty weight percent or at least about fifty volume percent cellulosic fibers including, but not limited to, cotton linters, rayon, bagasse, and more preferably wood pulps, such as softwoods (gymnosperms or coniferous) or hardwoods (angiosperms or deciduous), which fibers may be recycled. The balance of the fibers may be synthetic, such as polyolefin or polyester.

Cellulosic plies are frequently joined together by the use of an adhesive. Adhesive joining of cellulosic plies is advantageously described in commonly assigned U.S. Patent 5,143,776, issued September 1, 1992 to Givens, which patent is incorporated herein by reference.

However, adhesive joining of multiple cellulosic plies in a paper product can, and has, led to unsatisfactory performance. Particularly, paper products used as paper toweling, facial tissue, and bath tissue must have the proper ply bond strength. As used herein, "ply bond strength" refers to the force necessary to separate two adjacent plies from one another as described below.

Frequently tissue paper products, particularly paper toweling, are wetted in use. If the wet ply bond strength is insufficient, the plies separate in use and the paper product is destroyed. While it would seem an easy matter to simply increase the wet ply bond strength, the dry ply bond strength is directly coupled to the wet ply bond strength. In the prior art, as the wet ply bond strength increases to the proper level, the dry ply bond strength becomes too great. When the dry ply bond strength is too great, softness and absorbency are typically reduced.

Commonly assigned U.S. Patent application Serial No. 08/835,039, filed in the names of Neal, et al. on March 27, 1997 discloses combinations of nonionic adhesive materials that provide dry ply bond strength to such adhesively joined plies and cationic wet strength resins that provide wet ply bond strength. Such adhesive compositions have been found to provide adhesively laminated multi ply paper

products with adequate wet ply bond strength without having a dry ply bond strength that is too great.

It is also desirable to provide a user with a signal that such laminated paper toweling maintains its wet ply bond strength when the paper product becomes wetted during use. As is known in the art, many laminated paper towel products are provided with an aesthetically pleasing pattern of embossments with a laminating adhesive being disposed on the distal ends of such embossments for joining the plies together. It is also known that the pattern of embossments disappears when paper toweling becomes wetted. Commonly assigned U.S. Patent application Serial No. 08/749,708, filed in the names of Steinhardt, et al. on November 15, 1996 discloses the use of indicator means to maintain a pleasing pattern when paper toweling becomes wetted. One of the means disclosed therein is a laminating adhesive further comprising an opacifier, such as titanium dioxide. However, titanium dioxide pigment dispersions as are commonly available, also typically comprise an anionic polymer to aid in preventing such dispersions from flocculating and settling out. Combining such anionically stabilized dispersions with cationic wet strength resins as have been found to provide enhanced wet ply bond strength would result in an adhesive composition that further provides a visual signal of the enhanced wet ply bond strength. However, the incompatibility of anionic materials and cationic materials is well known in the art.

Thus there is a need for adhesive compositions that also comprise an anionically stabilized pigment dispersion that have improved enhanced wet ply bond strength. There is also a need for methods of blending anionically stabilized pigment dispersions and cationic wet strength resins to form such pigmented adhesive compositions. There is a still further need for pigmented adhesive compositions having minimal pigment particle agglomeration so as to maximize the opacifying power of such pigmented adhesive compositions and for methods capable of minimizing such agglomeration.

The Applicants have discovered certain compositions and methods that address such needs as will be readily apparent when considered in reference to the following description and when taken in conjunction with the accompanying examples.

### SUMMARY OF THE INVENTION

The present invention provides an adhesive composition suitable for laminating a multi-ply cellulosic paper product. The adhesive composition comprises a mixture of :

- (a) from about 2% to about 7% by weight of a water-soluble or water dispersible dry strength binder material;
- (b) from about 0.05% to about 5 % by weight of a water-soluble cationic wet strength resin;
- (c) from about 7% to about 30% by weight of an anionically stabilized pigment; and
- (d) from about 58% to about 91% by weight water.

The adhesive composition is preferably manufactured using energizing means that transfer at least about 5 watts per kilogram to the adhesive composition. Such transfer provides sufficient energy to the composition, as it is being manufactured, to effectively separate the cationic wet strength resin and the anionically stabilized pigment (i. e. the energizing means effectively maintains a positive charge density) minimizing agglomeration of the pigment particles and subsequent adhesive instability (e. g. coacervation).

All percentages, ratios, and proportions herein are by weight unless otherwise specified.

The present invention is described in more detail below.

### DETAILED DESCRIPTION OF THE INVENTION

While this specification concludes with claims particularly pointing out and distinctly claiming the subject matter regarded as the invention, it is believed that the

invention can be better understood from a reading of the following detailed description and of the appended example.

As used herein, the term "comprising" means that the various components, ingredients, or steps, can be conjointly employed in practicing the present invention. Accordingly, the term "comprising" encompasses the more restrictive terms "consisting essentially of" and "consisting of".

The present invention comprises pigmented adhesive compositions that are suitable for joining two or more plies of tissue so as to maximize the opacifying properties of the pigment, methods for producing such compositions, and paper products laminated using such compositions. The plies are cellulosic, as described below, and may be made according to the same manufacturing process, or according to different manufacturing processes.

#### The Plies

Each ply may have a plurality of embossments protruding outwardly from the plane of the ply towards an adjacent ply. The adjacent ply likewise may have opposing protuberances protruding towards the first ply. If a three ply paper product is desired, the central ply may have embossments extending outwardly in both directions, although a central ply having no embossments or unidirectional embossments may be feasible.

The plies may be made according to commonly assigned U.S. Patents 4,637,859, issued January 20, 1987 to Trokhan or 4,191,609, issued March 4, 1980 to Trokhan, which patents are incorporated herein by reference. Alternatively, the plies may be made using the uncreped, through air dried technology described in European Patent Application 0 617 164 A1, published on September 28, 1994 or conventionally dried using felts as is known in the art.

For the present invention, each ply may have a basis weight of about 8 to about 30 pounds per 3,000 square feet (13 to 48 g/m<sup>2</sup>), and preferably between about 11 and about 18 pounds per 3,000 square feet (18 and 29 g/m<sup>2</sup>), and preferably has a

composition of hardwood and/or softwood processed by any of the means well known in the art.

The fibers comprising the plies of the paper product are preferably cellulosic, such as cotton linters, rayon or bagasse; and more preferably are wood pulp, such as soft woods (gymnosperms or coniferous) or hard woods (angiosperms or deciduous). As used herein, a laminated paper product is considered "cellulosic" if the laminated paper product comprises at least about 50 weight percent or at least about 50 volume percent cellulosic fibers, including but not limited to those fibers listed above. The balance of the fibers comprising the laminated paper product may be synthetic, such as polyolefin or polyester. A cellulosic mixture of wood pulp fibers comprising softwood fibers having a length of about 2.0 to about 4.5 millimeters and a diameter of about 25 to about 50 micrometers, and hardwood fibers having a length of less than about 1.7 millimeters and a diameter of about 12 to about 25 micrometers has been found to work well for the laminated paper products described herein.

If wood pulp fibers are selected for the multi-ply paper products of the present invention, the fibers may be produced by any pulping process including chemical processes, such as sulfite, sulfate and soda processes; and mechanical processes such as stone groundwood. Alternatively, the fibers may be produced by combinations of chemical and mechanical processes or the fibers may be produced by a process which recycles waste paper products. The type, combination, and processing of the fibers used are not critical to the present invention. The hardwood and softwood fibers may be layered throughout the thickness of the laminated paper products or homogeneously blended therein.

#### The Adhesive Composition

The plies of the multi-ply paper product are adhesively joined together using a pigmented adhesive composition prepared according to the present invention. The adhesive composition is preferably applied to the embossments of at least one ply. Of course, the adhesive can be applied to the embossments of both plies. An adhesive according to the present invention comprises a mixture of a dry strength binder (e.g., a fully hydrolyzed polyvinyl alcohol adhesive), a cationic wet strength



resin (e.g., a thermosetting cationic resin), and an anionically stabilized titanium dioxide slurry. A particularly preferred adhesive composition comprises between about 58 and about 90 parts water, 2 to 7 parts dry strength binder solids, 0.05 to 5 parts cationic wet strength resin solids, and 7 to 30 parts titanium dioxide pigment. Each of these types of compounds will be described in detail below.

Importantly, to achieve satisfactory wet and dry ply bond strength and satisfactory signal intensity in the finished laminated tissue product of the present invention, the adhesive composition must be delivered to the plies at an appropriate level. Suitable delivery methods are discussed in the Ply Embossing and Lamination section below. It is also important that the components of the adhesive composition be delivered in the right proportions. One of skill in the art will recognize that the absolute concentrations of the solid components of the composition can be varied within certain limits (e.g. to control viscosity of the composition) as long as the adhesive solids delivered to the plies are sufficient to provide satisfactory wet and dry ply bond strength and satisfactory signal intensity. Specifically, it is important that the ratio of dry strength binder solids to cationic wet strength resin solids be within an acceptable range so as to provide adequate wet ply bond strength without having a dry ply bond strength that is too great. It is also important that the ratio of cationically charged material solids to anionically charged material solids be within an acceptable range so as to provide stable adhesive compositions having sufficient signal intensity.

Specifically, the Applicants have found that:

- 1) The ratio of dry strength binder solids to wet strength resin solids should not exceed about 6:1 in order to have an acceptable balance between wet ply bond strength and dry ply bond strength. Preferably, the ratio is less than about 4:1.
- 2) The ratio of anionically charged material solids to cationically charged material solids should be such that the charge density of the final adhesive composition is at least about 25 microequivalents per gram (as will be recognized by those having skill in the art, the specific weight ratios will depend on the charge density of the individual materials). For the preferred materials discussed herein, this

means the ratio of anionically charged pigment solids (pigment solids plus anionic suspension aid solids) to cationic solids (wet strength resin solids or other cationically charged solids added to maintain a net positive charge density) should be less than about 40:1. Preferably, the ratio of anionic solids to cationic solids is less than about 30:1. More preferably, the ratio is less than about 15:1.

#### Dry Strength Binder Materials

The adhesive composition of the present invention contains as an essential component from about 2% to about 7%, preferably from about 3.5% to about 6.5% by weight of a dry strength binder material chosen from the following group of materials: polyacrylamide (such as Accostrength 711 produced by CyTec Industries of West Paterson, NJ); starch (such as RediBOND 5320, 2005, and 3030) available from National Starch and Chemical Company, Bridgewater, NJ, or Amylose 1100, 2200 or Salvitose available from Avebe America, Princeton, NJ; polyvinyl alcohol (such as Evanol 71-30, supplied by the DuPont Corporation of Wilmington, DE); and/or guar or locust bean gums. Preferably, the dry strength binder materials are selected from the group consisting of polyvinyl alcohol, starch based resins, and mixtures thereof. The dry strength binder materials act to ensure that the multi-ply paper products of the present invention have adequate dry ply bond strength.

In particularly preferred adhesive compositions according to the present invention, the dry strength binder comprises polyvinyl alcohol. The polyvinyl alcohol component can be of any water-soluble or water-dispersible molecular weight sufficient to form an adhesive film. Generally, a weight average molecular weight of from about 40,000 to about 120,000, more preferably from 70,000 to 90,000 is preferred. Polyvinyl alcohol in solid form is commercially available under several trademarks such as ELVANOL<sup>®</sup> (DuPont), GELVATOL<sup>®</sup> (Monsanto) VINOL<sup>®</sup> (Air Products) and POVAL<sup>®</sup> (KURARAY). These grades have a degree of hydrolysis ranging from about 80 to about 100%. Those skilled in the art will appreciate that lowering the degree of hydrolysis and the molecular weight will improve water solubility but will reduce adhesion. Therefore the properties of the polyvinyl alcohol will have to be optimized for the specific application. A particularly preferred

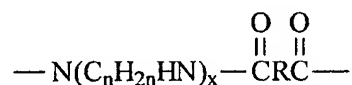
polyvinyl alcohol is Evanol 71-30, supplied by the DuPont Corporation of Wilmington, DE. Evanol 71-30 has a weight average molecular weight of about 77,000 and degree of hydrolysis of about 99%.

Alternatively, the dry strength binder can comprise a starch. In general, a suitable starch for practicing the present invention is characterized by water solubility or the ability to form stable dispersions that are hydrophilic. Exemplary starch materials include corn starch and potato starch, albeit it is not intended to thereby limit the scope of suitable starch materials. Waxy corn starch that is known industrially as amioca starch is preferred. Amioca starch differs from common corn starch in that it is entirely amylopectin, whereas common corn starch contains both amylopectin and amylose. Various unique characteristics of amioca starch are further described in "Amioca - The Starch from Waxy Corn", H. H. Schopmeyer, Food Industries, December 1945, pp. 106-108 (Vol. pp. 1476-1478). The starch can be in granular or dispersed form. One preferred starch, RediBOND, comes as a dispersed ready to use material. Granular starches such as Amylose 1100 are preferably sufficiently cooked to induce swelling of the granules. More preferably, the starch granules are swollen, as by cooking, to a point just prior to dispersion of the starch granule. Such highly swollen starch granules shall be referred to as being "fully cooked". The conditions for dispersion in general can vary depending upon the size of the starch granules, the degree of crystallinity of the granules, and the amount of amylose present. Fully cooked amioca starch, for example, can be prepared by heating an aqueous slurry of about 4% consistency of starch granules at about 190 °F (about 88 °C) for between about 30 and about 40 minutes. Other exemplary starch materials which may be used include modified cationic or anionic starches such as those modified to have nitrogen containing groups such as amino groups and methylol groups attached to nitrogen, available from National Starch and Chemical Company, (Bridgewater, NJ). Considering that such modified starch materials are more expensive than unmodified starches, the latter have generally been preferred.

Wet Strength Resin Materials

The adhesive composition of the present invention also contains as an essential component from about 0.05% to about 5.0%, preferably from about 0.1% to about 2.5% by weight of a wet strength resin material chosen from the following group of materials: polyamide-epichlorohydrin resins, glyoxalated polyacrylamides resins, styrene-butadiene latexes; insolubilized polyvinyl alcohol; urea-formaldehyde; polyethyleneimine; chitosan polymers and mixtures thereof. Preferably, the wet strength resins are water-soluble cationic resins selected from the group consisting of polyamide-epichlorohydrin resins, glyoxalated polyacrylamide resins, polyethyleneimine resins, and mixtures thereof.

Polyamide-epichlorohydrin resins are cationic wet strength resins which have been found to be of particular utility. Preferably, the polyamide-epichlorohydrin resin comprises a water-soluble polymeric reaction product of epichlorohydrin, and a water-soluble polyamide having secondary amine groups. The ratio of epichlorohydrin to secondary amine groups of said polyamide is preferably from about 0.5 to 1 to about 2 to 1. Preferably, the water-soluble polyamide is derived from reacting a polyalkylene polyamine and a saturated aliphatic dibasic carboxylic acid containing from about 3 to 10 carbon atoms. Preferably the mole ratio of polyalkylene to dibasic carboxylic acid is from about 0.8 to 1 to about 1.5 to 1. Preferably the saturated aliphatic dibasic carboxylic acid is adipic acid and the polyalkylene polyamine is diethylene triamine. Most preferably, the water-soluble polyamide contains recurring groups of the formula



wherein n and x are each 2 or more and R is the divalent hydrocarbon radical of the dibasic carboxylic acid containing from about 3 to 10 carbon atoms. Resins of this type are commercially available under the trademarks KYMENE® (Hercules, Inc.) and CASCAMID® (Borden). An essential characteristic of these resins is that they are phase compatible with the polyvinyl alcohol, i.e., they do not phase-separate in the presence of aqueous polyvinyl alcohol.

Suitable types of such resins are described in U.S. Patent No. 3,700,623, issued on October 24, 1972, and 3,772,076, issued on November 13, 1973, both issued to Keim and both being hereby incorporated by reference. One commercial source of a useful polyamide-epichlorohydrin resin is Hercules, Inc. of Wilmington, DE, which markets such resins under the trademarks Kymene<sup>®</sup> 557H Kymene<sup>®</sup> 557LX, and Kymene<sup>®</sup> 557ULX, with Kymene<sup>®</sup> 557LX being preferred.

Base-activated polyamide-epichlorohydrin resins which are also useful in the present invention are also sold by Hercules, Inc. of Wilmington, DE, which markets such resin under the trademark Kymene<sup>®</sup> 450. Other examples of commercial sources of base-activated polyamide-epichlorohydrin resins are sold under the Santo Res trademark, such as Santo Res 31, by Monsanto Company of St. Louis, MO. These types of materials are generally described in U.S. Patent Nos. 3,855,158 issued to Petrovich on December 17, 1974; 3,899,388 issued to Petrovich on August 12, 1975; 4,129,528 issued to Petrovich on December 12, 1978; 4,147,586 issued to Petrovich on April 3, 1979; and 4,222,921 issued to Van Eenam on September 16, 1980, all incorporated herein by reference.

Glyoxalated polyacrylamide resins have also been found to be of utility as wet strength resins. These resins are described in U.S. Patent No. 3,556,932, issued on January 19, 1971, to Coscia, et al. and 3,556,933, issued on January 19, 1971, to Williams et al., both patents being incorporated herein by reference. One commercial source of polyacrylamide resins is Cytec of Stanford, CT, which markets one such resin under the trademark Parex<sup>™</sup> 631 NC.

Still other water-soluble cationic resins finding utility in this invention are urea formaldehyde and melamine formaldehyde resins. The more common functional groups of these polyfunctional resins are nitrogen containing groups such as amino groups and methylol groups attached to nitrogen. Polyethylenimine type resins may also find utility in the present invention.

Pigment

As discussed in the Background of the Invention section above, it is desirable to provide a user with an indication that desirable properties, such as wet ply bond strength, are maintained when adhesively laminated paper products are wetted. Also as noted above and described in aforementioned U.S. Patent application Serial No. 08/749,708, the disclosure of which is incorporated herein by reference, laminating adhesive compositions comprising a pigment can provide such a signal.

As is well known, refractive index is one major factor determining the opacifying efficiency of a pigment. Table 1 below compares the refractive index of pigments commonly used in the paper industry.

Table 1

<u>Compound</u>	<u>Refractive Index</u>
Titanium Dioxide	
Rutile	2.72
Anatase	2.55
Zinc Oxide	2.02
Kaolin Clays	
Filler	1.57
Calcined	1.57
Calcium Carbonate	
Natural Ground	1.56
PCC-Calcite	1.66
Talc	1.57
Precipitated Silica	1.45

To be suitable for use as a pigment for purposes of the present invention, such inorganic pigmenting materials should have a refractive index greater than about 1.4. Preferably, the refractive index is greater than about 1.7. Particularly preferred inorganic pigmenting materials have a refractive index greater than about 2.0.

In addition to refractive index, the particle size of an opacifier also has a major effect on the opacity of the adhesive compositions of the present invention. That is, for a given concentration of pigment in an adhesive composition, compositions comprising pigments having a smaller particle size will be more opaque. Pigments suitable for use in the present invention have a median, unsonicated particle size less than about 1.4 microns. Preferably, the median particle size is less than about 0.8 microns. More preferably, the median particle size is less than about 0.6 microns. A method for measuring median unsonicated particle size is given in the TEST METHODS section below.

A particularly preferred pigmenting material is titanium dioxide ( $\text{TiO}_2$ ). Two crystalline forms of  $\text{TiO}_2$  exist: anatase and rutile. The rutile form is the most opaque due to its higher refractive index. In the papermaking art it is known that a given opacity can typically be achieved with about 15–20% less rutile than anatase. Titanium dioxide is commercially available in both a dry powder form and as a slurry in water. For purposes of the present invention, the water slurry form is preferred because of ease of mixing with other components of the present adhesive composition and because the pigment particles are more fully dispersed so as to provide better opacity.

In order that  $\text{TiO}_2$  remain suspended, additional components are included in commercially available  $\text{TiO}_2$  slurries. In particular, dispersion aids are used to insure that suspended  $\text{TiO}_2$  particles do not flocculate and settle out. Dispersion aids are of two types: stearic stabilizers and electrostatic stabilizers. Stearic stabilizers surround the suspended  $\text{TiO}_2$  particles with an adsorbed layer of a polymer. Stearic interaction between the polymer layers on different particles prevents the particles from approaching closely enough such that they can agglomerate. Typically, stearically stabilized slurries are quite viscous because of the adsorbed layer of polymer. Titanium dioxide particles also can be stabilized electrostatically by surrounding them with a charged species. Such species can be either cationic or anionic. Because most  $\text{TiO}_2$  is used by the paint and paper industries which both require anionic slurries for their processes, cationic  $\text{TiO}_2$  slurries are uncommon. An example of a suitable anionic electrostatic suspension aid is the sodium polyacrylate

described in U.S. Patent 4,503,172, issued in the name of Farrar, et al. on March 5, 1985. Such a material is available as Dispex N40V manufactured by from Allied Colloids of Suffolk, VA.

A suitable, commercially available  $\text{TiO}_2$  slurry is Ti-Pure<sup>®</sup> RPS Vantage Rutile Paper Slurry which is available from the DuPont Company of Wilmington, DE. This material is an anionically stabilized slurry of the rutile form of  $\text{TiO}_2$  in water having a nominal  $\text{TiO}_2$  solids level of 71.5%. The median unsonicated particle size of this material is typically less than 0.5 microns.

Such a  $\text{TiO}_2$  slurry has been found to provide a visual signal of desirable wet in use properties when the  $\text{TiO}_2$  pigment is used according to the present invention. The Applicants have found that pigmented adhesive compositions according to the present invention should comprise at least about 7%  $\text{TiO}_2$  solids to provide a satisfactory visual signal of desirable wet properties.  $\text{TiO}_2$  solids levels greater than about 30% provide no additional improvement in signal intensity. Preferably, the  $\text{TiO}_2$  solids level should be between about 10% and about 30%. More preferably, the  $\text{TiO}_2$  solids level is between about 15% and about 25%. One of skill in the art will recognize that, if other pigments are used, the level of pigment will need to be adjusted to provide a satisfactory visual signal. As noted above, relative refractive index between  $\text{TiO}_2$  and a potential replacement pigment can provide an initial indication of how great an adjustment is needed.

Alternatively, organic pigmenting means, such as Ropaque HP91 from Rohm & Haas Corp., Philadelphia, PA, may be used to replace at least part of the titanium dioxide. Such organic pigmenting means are hollow polymeric spheres that are provided as a water emulsion. Since the spheres are hollow, light is bent multiple times as it passes through a dispersion of such pigments. This multiple bending provides an apparent refractive index that provides hiding power comparable to  $\text{TiO}_2$ . Since, such organic pigmenting means are also anionically stabilized, the same issues of incompatibility with cationic wet strength resins that are discussed above also affect the stability and opacity of adhesive compositions comprising organic pigmenting means.



An alternative inorganic pigmenting means that may be used as a substitute for at least part of the titanium dioxide in adhesive compositions of the present invention is silica (e. g. fumed silica, colloidal silica, and the like). A suitable fumed silica is AEROSIL 300® which is available from Degussa Corp. of Ridgefield Park, NJ. As is clearly evident from Example 5, pigmented adhesive compositions comprising such alternative inorganic pigmenting means provide desirable turbidity and viscosity as are discussed above. The Applicants further believe that replacing part of the titanium dioxide with silica has the potential to reduce wear in adhesive compounding and application apparatus because of the small ultimate particle size of the silica particles. For example, the AEROSIL 300® discussed above has an ultimate particle size of 7 nanometers compared to 0.5 microns for the TiO<sub>2</sub> pigment discussed above.

#### Optional Cationic Additives

As is well known cationic species carry a positive charge and anionic species carry a negative charge. One measure of such charges is charge density. A method for measuring charge density is provided in the TEST METHODS section below. The Applicants have found that suitable adhesive compositions according to the present invention should have a positive charge density. That is, a suitable adhesive composition according to the present invention is at least slightly cationic (positive charge density). The Applicants believe that one of the benefits of the method of the present invention is that energizing one of the anionic or the cationic components of the composition before beginning to add the other component prevents a situation wherein portions of the blend have a negative charge density during addition of the remaining charged components of the composition (Such negative charge density, when the components are mixed under low energy conditions, has been found to increase the risk of coacervation, separation and loss of opacifier efficiency). By providing sufficient energy to the mixing step, formation of substantial portions of the blend having a negative charge density and the resulting coacervation are significantly reduced.

Table 2 lists charge density values for representative components suitable for use in the adhesive composition of the present invention.

Table 2

<u>Component</u>	<u>Charge density</u> (Microequivalents/gram)
Cationic Materials	)*
Kymene® 557 LX	
RediBond® 5320	+3243
Anionic Material	+264
TiO <sub>2</sub> Slurry (Ti-Pure® RPS)	
	-48

\* 100% solids basis

The relative amounts of such components in a composition will determine the charge density of the composition. For example, a composition comprising about 1.5% Kymene 557LX and about 23% TiO<sub>2</sub> prepared according to the method of the present invention has been found to have a charge density of about +185 microequivalents per gram. On the other hand, a composition comprising about 0.3% Kymene 557LX and about 23% TiO<sub>2</sub> has been found to have a charge density of about -1.7 microequivalents per gram. Preferably, the charge density in the finished pigmented adhesive composition is at least about +25 microequivalents per gram of dispersed solid material. Preferably, the charge density is at least about +30 microequivalents per gram, more preferably, at least about +50 microequivalents per gram.

As will be discussed below, the method of the present invention is particularly efficient in minimizing pigment agglomeration in pigmented adhesive compositions prepared thereby. However, it is still necessary to maintain a minimum positive charge density in the finished adhesive composition so as to maximize stability of the composition. For example, a particular adhesive composition may not comprise enough cationic wet strength resin to maintain a positive charge density which increases the risk of coacervation and agglomeration. To compensate for such

insufficient positive charge density, materials having a positive charge density (i. e. cationic additives) may be added to the composition, if the charge density contribution from cationic materials in the composition is insufficient. Suitable materials include: cationic starches (such as Celquat L200 as is available from National starch and Chemical Co. of Bridgewater, NJ) and quaternary ammonium compounds (such as are available from Witco Chemical Co. of Dublin, OH as DP-SC-505-91). A particularly preferred cationic additive is a relatively low molecular weight polyamine having a high charge density. A particularly preferred material of this type is Cypro<sup>®</sup> 515 which has a charge density of about +6400 microequivalents per gram (100% solids basis) and is available from Cytec of Stamford, CT as. For example, when 0.6% Cypro<sup>®</sup> 515 is added to a 0.3% Kymene<sup>®</sup> 557 LX solution prior to addition of the TiO<sub>2</sub>, the composition, after addition of the TiO<sub>2</sub>, has a charge density of +35 microequivalents per gram rather than -1.7 microequivalents per gram described above. Such a charge density has been found to provide an adequately stable suspension for use as a laminating adhesive.

#### Adhesive Manufacture

As noted above, a preferred wet strength resin, Kymene<sup>®</sup>, is highly cationic and, therefore, when Kymene<sup>®</sup> is combined with anionically stabilized TiO<sub>2</sub> slurries it can react with anionic components of the adhesive composition, such as an anionically stabilized pigment dispersion, causing stratification and separation of the adhesive composition due to coacervation. Example 1 below demonstrates this behavior.

Surprisingly, the Applicants have found that, by appropriately blending the above identified components, the well known difficulties of producing stable compositions combining cationic and anionic materials can be overcome.

Specifically, the Applicants have found that by using the method described in detail below, wherein one of the anionic or the cationic component of the composition is energized before the other of the components are added, remarkably stable pigmented adhesive compositions can be produced. A liquid material is "energized" if an "energizing means" is capable of providing at least about 5 watts per kilogram

as the liquids are being blended. Preferably, the energizing means should be capable of delivering at least about 15 watts per kilogram as the liquids are being blended. More preferably, the energizing means is capable of delivering at least about 25 watts per kilogram as the liquids are being blended. A method of determining the energy delivered (watts per kilogram) is provided in the TEST METHODS section.

Suitable energizing means include: batch mixers providing a high agitator tip speed, for example blenders as are available from Sunbeam Corp. of Delray Beach, FL with the brand name Osterizer; rotor/stator high shear mixers, as are available from Charles Ross & Son, Hauppauge, NY; and in line mixers such as are available from Quadro Inc., Millburn, NJ as model Quadro ZC. A particularly preferred energizing means is the Breddo Likwifier, Model LOR as supplied by Breddo Likwifier of Kansas City, MO.

Further, the Applicants have found that, when such methods are used, the median particle size of the pigment in the finished adhesive composition is comparable to the median unsonicated particle size of the pigment in the original pigment dispersion. That is, the method of the present invention utilizes such pigment dispersions in a highly efficient manner so as to provide the adhesive composition with maximum opacity.

This efficiency is shown very clearly in Table 3 which compares the turbidity (turbidity is a measure of opacity—a method to measure turbidity is provided in TEST METHODS section) of pigmented adhesive compositions prepared according to the methods described in Examples 1 and 2 below.

Table 3

	Median Unsonicated	
	<u>Turbidity</u>	<u>Particle Size</u>
	(NTU)	(microns)
Composition prepared according to method of Example 1	1217*	Two peaks (2.2, 17.1)
Composition prepared accord-	3467*	0.5

ing to method of Example 2

\*Measured at a concentration of 0.5 grams of adhesive in 1000 milliliters of water

As can be clearly seen, the adhesive composition prepared according to the method of Example 2 (method of the present invention) has a substantially higher turbidity (greater opacity) and lower median particle size than the adhesive composition prepared according to the method of Example 1 (low energy mixing).

Without being bound by theory, the Applicants believe that energizing one of the charged components of the composition prior to adding the component having the opposite charge keeps the pigment particles sufficiently separated so that agglomeration of pigment particles (with the resulting increase in mean pigment particle size) is minimized. The Applicants have found that, when pigmented adhesive compositions are prepared according to the present invention, the pigment particles in such compositions have a mean unsonicated particle size no greater than about 2.5 times the mean unsonicated particle size of the pigment in the pigment dispersion. Typically, the mean unsonicated particle size of the pigment in the pigmented adhesive composition is less than about 1.5 times the mean unsonicated particle size of the pigment in the pigment dispersion. The Applicants further believe that providing sufficient mechanical energy while the second component is being added to the first minimizes interactions between anionic and cationic species. That is, coacervation, and the resulting substantial increase in the viscosity of the composition (i. e., stratification and gelling), is minimized.

While, as noted above, energizing a first component of the adhesive composition prior to adding any of the other components meaningfully minimizes coacervation and pigment particle agglomeration, addition order can affect the properties of the final adhesive composition. The following describes a particularly preferred method of preparing the adhesive compositions of the present invention.

The first step of this preferred method is to provide the requisite quantity of a suitable cationic wet strength resin. For example to prepare 100 parts of the preferred adhesive compositions of the present invention between about 0.05 parts

and about 5 parts of a polyamide-epichlorohydrin resin may be provided. Preferably, this resin is in a solution comprising between about 10 % by weight and about 15 % by weight resin solids. A particularly preferred method provides about 12 parts of a 12.5 % by weight a polyamide-epichlorohydrin resin solution. Optionally, if the desired concentration of cationic wet strength resin is too low to maintain a suitable charge density (see discussion above), one of the alternative cationic materials discussed above may be provided prior to energizing the cationic wet strength resin solution.

This polyamide-epichlorohydrin resin solution is then energized by suitable means of providing mechanical energy thereto as described above. It is important that sufficient energy be provided by this energizing step cause the resin solution to become turbulent. For example, the resin solution should not be so highly viscous that a substantial portion of the mechanical energy provided is converted into thermal energy causing the temperature of the solution to rise substantially. Specifically, the viscosity of the resin solution should be less than about 500 centipoise when measured according the method described in the TEST METHODS section below. More preferably, the viscosity should be less than about 300 centipoise.

As noted above, suitable energizing means are capable of providing at least about 5 watts per kilogram of energy to the resin solution provided by the first step. A particularly preferred energizing means for purposes of the present invention is the Breddo Likwifier, Model LOR.

After energizing the cationic wet strength resin solution, the pigment dispersion is added thereto. To produce 100 parts of the preferred pigmented adhesive composition described above between about 7 and about 30 parts of the pigment dispersion are added while continuing to provide energy to the liquid. For the particularly preferred  $\text{TiO}_2$  dispersion discussed above, about 32 parts of the 71.5 percent by weight dispersion are added.

Preferably, the pigment dispersion is added at a rate so as to insure that the bulk of the material in the mixing zone comprises the cationic wet strength solution or a

dispersion of pigment in the cationic wet strength resin solution. Otherwise, there may be insufficient energy to maintain separation of the pigment particles and minimize coacervation. As used herein, the term "mixing zone" is determined by the geometry of specific energizing means chosen and is that volume where energy is transferred from the energizing means to the liquid or dispersion being energized. The Applicants have found that a useful measure of addition rate is a Delivery Number. As used herein "Delivery Number" is a dimensionless number which depends on the addition rate of pigment dispersion, the geometry of the agitator, and the rotational velocity of the agitator and can be calculated according to the following equation:

$$Q = \frac{\left( \frac{PigWt}{AddnTime} \right)}{nd^3 \rho}$$
$$n = \frac{RotVel}{60}$$

where:

Q = Delivery Number

PigWt = Weight of pigment dispersion added (Kg)

AddnTime = Time required to add pigment (seconds)

r = Pigment dispersion density (g/cm<sup>3</sup>)

RotVel = Rotational velocity of agitator (rpm)

d = Diameter of agitator (cm)

For example, in preparing a batch of the pigmented adhesive composition of the present invention the following data were taken:

PigWt = 36.97 Kg;

AddnTime = 240 seconds

$r = 2.2 \text{ g/cc}$  ( $\text{TiO}_2$  slurry, comprising about 72%  $\text{TiO}_2$  solids)

RotVel = 1800 rpm

$d = 24.3 \text{ cm}$

The resulting Delivery Number is  $1.63 \times 10^{-4}$ . As can be seen from Example 3, such a Delivery Number indicates that the pigment dispersion was added to the mixing zone sufficiently slowly to prevent agglomeration (i.e. the median unsonicated particle size is substantially less than 1 micron).

The last required step in this preferred method is to add the dry strength binder solution (still continuing to provide energy to the liquid). The dry strength binder solution is preferably added after the other components because such solutions typically have a high viscosity and energizing such solutions without an unacceptable temperature increase is difficult. As noted above, the dry strength binder solution preferably comprises a starch based resin or polyvinyl alcohol in water. Preferably, the concentration of dry strength binder in such a water solution is between about 2% and about 14% and between about 2 and about 7 parts of binder solids are added to the adhesive composition when preparing 100 parts of the finished adhesive composition.

Optionally, other components may be added after blending the above materials. For example, a portion of dilution water could be held back to allow for final viscosity and solids level control to compensate for lot to lot variation in the individual raw materials.



### Alternative Adhesive Manufacturing Methods

#### Addition Order

While the method described above is preferred because it provides maximum dispersion of the pigment particles and minimizes particle agglomeration, alternative methods, particularly alternative addition orders, are also within the scope of the present invention. For example, an addition order comprising the following steps: 1) providing a dry strength binder solution; 2) energizing the dry strength binder solution; 3) providing an anionically stabilized pigment dispersion; 4) mixing the pigment dispersion into the dry strength binder solution to form a pigmented binder blend; 5) providing a cationic wet strength resin solution; and 6) mixing the wet strength resin solution into the pigmented binder blend is also contemplated by the Applicants. Pigmented adhesive compositions prepared according to this alternative method have substantially improved opacity, agglomeration reduction and stability when compared to low energy mixing methods. Specifically, the median unsonicated particle size for an adhesive composition comprising the preferred TiO<sub>2</sub> pigment discussed above is about 1.0 microns and the initial separation time is greater than 24 hours. When these results are compared to the results shown in Table 2 above the improvement over the low energy mixing method of Example 1 is obvious.

#### Energizing Means

An alternative energizing means, suitable for purposes of the present invention, is a mixer that provides energy to a liquid medium by forming ultrasonic vibrations therein (A suitable apparatus is produced by Sonic Corp. of Stratford, CT as the Sonolator). The Sonolator is an in-line system that provides ultrasonic vibrations by pumping a liquid, a blend of liquids, or a solid dispersion in a liquid through a shaped orifice at a high linear velocity. The liquid stream impinges against a blade cantilevered in the stream. Flow over the blade causes vibrations in the blade which produces cavitation in the stream converting flow energy into mixing/dispersion energy.

### Ply Embossing and Lamination

After the papermaking process which forms a ply is complete, one or more plies may be embossed and laminated. Embossing/lamination is one means of obtaining a pattern that is useful in providing a visual indication of desirable properties when the embossing/lamination steps are carried out using the pigmented adhesive composition of the present invention.

Embossing may be accomplished according to the knob-to-knob embossing process illustrated by commonly assigned U.S. Patent 3,414,459, issued December 3, 1968 to Wells; the nested embossing process illustrated in U.S. Patent 3,556,907, issued January 19, 1971 to Nystrand; or a dual ply process illustrated in commonly assigned U.S. Patent 5,294,475, issued March 15, 1994 to McNeil, all of which patents are incorporated herein by reference.

For the embodiments described and claimed herein, the embossments may be spaced on a pitch of 0.05 to 0.70 inches and may have an area at the distal end ranging from 0.001 to 0.100 square inches. Each embossment may be made on a roll having knobs which protrude 0 to 0.120 inches from the plane of the roll. The embossments may be round, oval shaped, or irregularly shaped.

Each of the embossments has a distal end and the adhesive composition of the present invention is applied at least a portion of the distal ends to form a laminated tissue product according to the present invention. Preferably the adhesive solids are applied at a rate of between about 12 and about 20 pounds of adhesive solids per ton paper (6 to 10 grams of adhesive solids per kilogram of paper) of to at least some of the distal ends on at least one of the tissue plies to form the laminated tissue product. More preferably between about 14 pounds of adhesive solids per ton of paper and about 18 pounds of adhesive solids per ton of paper (7 grams per kilogram to 9 grams per kilogram) are applied. As used herein, the term "adhesive solids" is intended to mean the nonaqueous components of the adhesive composition of the present invention and includes wet strength resins dry strength additives, TiO<sub>2</sub>, and any dispersion aids or other solid materials that may be added to the adhesive composition.

A particularly preferred method of embossing and laminating a to produce laminated tissue products according to the present invention is described in Example 4.

The Applicants believe that the following non-limiting examples are illustrative of the present invention.

#### EXAMPLES

##### Example 1

This example is intended to illustrate the properties of a coacervated mixture of a cationic wet strength resin, and anionically stabilized pigment dispersion and a dry strength binder solution made using a conventional mixing method.

A pigmented adhesive composition was prepared according to the following method:

1) provide about 13 parts of a cationic wet strength resin solution comprising about 12.5% Kymene<sup>®</sup> 557LX resin solids and having a pH of about 3.0; 2) begin agitation of the wet strength resin solution using a Lightnin Model TS2010 mixer, which is available from Lightnin of Rochester, NY. Such a mixer provides about 1.7 watts per kilogram of power to the solution; 3) with continued agitation add about 23 parts of a 72% solids TiO<sub>2</sub> dispersion (Ti-Pure<sup>®</sup> RPS Vantage Rutile Paper Slurry from DuPont) having a pH of about 8.4; 4) add about 64 parts of a dry strength additive (ELVANOL 71-30 from DuPont) solution having about 7.4% resin solids with continued mixing; and 5) add water as necessary with continued mixing to provide 100 parts.

Table 4 lists property data obtained on evaluation of this adhesive composition.

Table 4

<u>Property</u>	<u>Value</u>
pH	4.3
Median Unsonicated Particle Size ( $\mu$ )	
First Peak	17.1
Second Peak	2.2
Turbidity	1217
Initial Separation Time	4 Hours

\*Measured at a concentration of 0.5 grams of adhesive in 1000 milliliters of water

#### Example 2

This example uses the same materials, concentrations, and addition order as Example 1 but uses the method of the present invention to provide a pigmented laminating adhesive composition suitable for joining two or more plies of tissue paper. Specifically, a laboratory blender (Osterizer as is available from Sunbeam Corp. of Delray Beach FL) was used which energizes the liquid with about 110 watts per kilogram.

Table 5 lists property data obtained on evaluation of this adhesive composition.

Table 5

<u>Property</u>	<u>Value</u>
pH	4.3
Median Unsonicated Particle Size ( $\mu$ )	0.5
Turbidity	3467
Initial Separation Time	>4 Weeks

#### Example 3

This example is intended to demonstrate the use of commercial scale mixing equipment to prepare pigmented adhesive compositions according to the present invention.

#### Apparatus:

Mixer Breddo Likwifier, Model LOR, Size 50 gallon, 30 Hp motor,, adjustable speed (640–2300 rpm) as is available from Breddo Likwifier of Kansas City, MO

Impeller 1) Standard Disk—Part No. 8-711-0004  
2) Toothed Disk—Part No. 8-711-0691

## Composition

<u>Component</u>	<u>%</u>
Cationic Wet Strength Resin Solution	12
TiO <sub>2</sub> Dispersion	32
Dry Strength Additive Solution	55
Water	1
Total	100

Table 6 lists the properties of several pigmented adhesive batches made according to various process conditions.

Table 6

<u>Run</u>	<u>Disk</u>	<u>Batch</u>	<u>Speed</u>	<u>Delivery</u>	<u>Energy Added</u>	<u>Median Unsonicated</u>	<u>Turbidity</u>
<u>No.</u>	<u>Type</u>	<u>Size</u>	<u>(rpm)</u>	<u>Number</u>	<u>(Watt/Kg)</u>	<u>Particle Size</u>	<u>(NTU)</u>
		(Kg)				(m)	
1	Standard	116	1800	$1.62 \cdot 10^{-4}$	35.2	0.679	3567
2	Toothed	116	1800	$1.62 \cdot 10^{-4}$	90.3	0.566	3721
3	Toothed	230	1800	$5.15 \cdot 10^{-4}$	88.1	0.577	NA

Example 4

This example discusses the properties of a multi-ply paper product laminated using the pigmented adhesive composition prepared according to the method of Example 2.

Such paper products may be made from two plies of cellulosic fibers as is commonly used in Bounty brand paper towels marketed by The Procter & Gamble Company of Cincinnati, OH and the assignee of the present invention. Each ply is made of 65 percent northern softwood Kraft, 35 percent CTMP, and has a basis weight of 14 pounds per 3,000 square feet. Each ply is embossed in a nested embossing process by elliptically shaped protuberances having at the distal end a major axis of 0.084 inches, a minor axis of 0.042 inches and a protuberance height of 0.070 inches. The

protuberances are spaced in a concentric diamond pattern on a 45 degree pitch of about 0.118 inches. Two complementary plies are made and joined together at a zero clearance marrying nip, so that a unitary laminate having about 33 protuberances per square inch per ply is formed.

The method of Example 3 provides an adhesive composition having 5.75% total adhesive solids, of which 1.5% is Kymene<sup>®</sup> and 4.25% is polyvinyl alcohol. The adhesive composition also comprises 23% TiO<sub>2</sub> solids. This adhesive composition is applied to the protuberances of one ply. The total solids of the adhesive composition is applied to the paper product. The resulting paper product has a wet ply bond strength of 5.5 grams per inch and a dry ply bond strength of 10.4 grams per inch. Methods for measuring wet ply bond strength and dry ply bond strength are described in the TEST METHODS section below.

In Table 7 the wet ply bond strength and the dry ply bond strength of paper towel products laminated with adhesive compositions prepared according to the present invention are compared to other commercially available paper towels.

Table 7

<u>Sample</u>	<u>Manufacturer</u>	Wet Ply Bond	Dry Ply bond
		<u>Strength</u> (grams/inch)	<u>Strength</u> (grams/inch)
Present Invention	Assignee	5.5	10.4
BOUNTY	Assignee	3.9	10.1
BRAWNY*	James River	3.1	10.1
SPARKLE*	Georgia Pacific	3.0	7.0
MARDIS GRAS*	Ft. Howard	3.4	7.6
VIVA 2-PLY*	Scott	3.0	4.4
HI-DRI*	Kimberly Clark	3.4	5.5

\* Data from U.S. Patent Application Serial No. 08/835,039

Each of the wet and dry ply bond strengths in Table 6 represents an average of at least five samples. Of course, for the dry ply bond strength test, each of the five

samples represents an average of four test specimens. As is clearly demonstrated by the data shown in Table 7, the adhesive composition of the present invention provides substantially improved wet ply bond strength while maintaining a dry ply bond strength comparable to commercially available paper towels. When paper towels that are laminated using the adhesive compositions of the present invention are immersed in water, the pattern of the pigmented adhesive is clearly visible. When the commercially available paper towels listed in Table 7 are similarly immersed, there is no clearly visible pattern.

#### Example 5

This example is intended to demonstrate the formulation of a pigmented laminating adhesive according to the present invention that comprises alternative materials. Table 8 lists the composition of a laminating adhesive according to the present invention that comprises both an alternative inorganic pigmenting material and an optional cationic additive.

Table 8

<u>Component</u>	<u>Concentration</u> (Weight Percent)
Dry Strength Additive <sup>1</sup>	4.5
Pigment <sup>2</sup>	18.0
Cationic Wet Strength Resin <sup>3</sup>	0.3
Optional Cationic Additive <sup>4</sup>	0.7
Alternative Pigment <sup>5</sup>	1.0
Water	QS 100%

1. ELVANOL<sup>®</sup> 71-30
2. Solids provided by Ti-Pure<sup>®</sup> RPS Vantage Rutile Paper Slurry
3. Kymene<sup>®</sup> 557LX
4. Cypro<sup>®</sup> 515
5. Aerosil<sup>®</sup> 300

The composition is prepared substantially according to the preferred method of the present invention using a laboratory blender (Osterizer) to energize the composition as the components are blended. Evaluation of the finished composition shows: 1) no visible separation after 14 days; 2) turbidity comparable to other compositions of the present invention—2600 NTU; 3) the whiteness of a thin layer of the adhesive composition of the present example, when the composition is applied to a tissue substrate using metering rods (available from Paul N. Gardner Co., Inc. of Pompano Beach, FL as size 8 ) to control coating thickness, is comparable to the whiteness of an adhesive composition prepared according to Example 2 applied to a tissue substrate in the same manner, and 4) viscosity is comparable to other compositions of the present invention—170 centipoise.

## TEST METHODS

### Dry Ply Bond Strength

Samples of four finished paper products are provided. Samples are aged for at least two weeks after making to allow the adhesive system to fully cure. One three inch strip running the entire length of the sample is cut from the center of each sample. Two of the strips are cut in the machine direction and the other two are cut in the cross machine direction (i.e., between perforations in the machine direction or between edges in the cross machine direction). The strips are separated slightly along either of the three inch edges, so that each ply is available independent of the other. The plies are manually separated until the sample has a gage length of two inches.

Each ply is placed in the jaw of a tensile machine. A suitable tensile tester is a Model 1451-24 supplied by the Thwing/Albert Corporation of Philadelphia, Pennsylvania. The crosshead separation speed is set at 20 inches per minute and travels 7.5 inches from an initial separation of 2.0 inches. Data is only recorded for the last six inches of crosshead travel. All four samples are tested in tension. The four numbers are then averaged to give a single ply bond strength representative of the product from which all four samples were taken.



Care must be taken that the portion of the sample yet to be separated by the tensile machine does not contact the lower jaw or the lower crosshead of the tensile machine. If such contact occurs, it will register on the load cell and give a reading which is erroneously high. Similarly, care must be taken that the portion of the sample yet to be separated does not contact the portion of the sample having the plies already separated by the tensile tester. If such contact occurs, it will falsely increase the apparent ply bond strength. If either of the aforementioned contacts occur, the data point is to be discarded and a new sample tested.

#### Wet Ply Bond Strength

Samples of four finished paper products are provided. Samples are aged for at least two weeks after making to allow the adhesive system to fully cure. One three inch strip running the entire length of the sample (e.g., between perforations for material that has been converted into commercial paper toweling) is cut from the center of each sample. Two of the strips are cut in the machine direction and the other two are cut in the cross machine direction (i.e., between perforations in the machine direction or between edges in the cross machine direction). The strips are separated slightly along either of the three inch edges, so that each ply is available independent of the other. The plies are manually separated until the sample has a gage length of two inches.

The plies are separated along one of the three inch edges of the sample. The portion of the sample which has not been separated, i.e., the portion which is not to be placed in the jaws of the tensile machine, is immersed in distilled water. After immersion, the sample is immediately removed from the water and allowed to drain for 60 seconds on a draining rack. The draining rack is provided with a nylon wire square mesh. The wires forming the mesh are 0.015 inches diameter on a pitch of 0.25 inches. The drying rack is oriented at an angle of 45 degrees relative to the horizontal. While drying on the drying rack, the sample is oriented so that the longer edges of the sample are downwardly aligned with the slope of the drying rack. The separated edges of the ply are brought back together in the drying rack so that the sample is as smooth as possible, and the sample properly drains excess water. After

having been prepared in this manner, the sample is then tested in the tensile machine as described above for the dry ply bond strength.

### Viscosity

#### Overview

This method is suitable for measurement of viscosity as a function of shear rate. The sample is disposed in a narrow annular volume between two concentric cylinders. The inner cylinder rotates at a controlled angular speed, and the resulting torque or force generated by the sample between the two cylinders is a measure of the viscosity of the sample disposed between them.

#### Apparatus

**Viscometer** A suitable viscometer is available from Paar Physica USA, Inc. of Edison, NJ as Model MC1.

#### Apparatus Set Up

- 1) Set up the viscometer according to the manufacturer's instructions.
- 2) Sample and apparatus temperature should be  $23 \pm 1^\circ\text{C}$ .

#### Method

- 1) Fill the outer cylinder to the marked level with the sample to be evaluated.
- 2) Insert the outer cylinder into the viscometer insuring that the inner cylinder is centered therein and lock the outer cylinder into place. Allow at least ten seconds after locking the outer cylinder into place for the sample to fill the annular volume between the two cylinders before beginning a viscosity scan.
- 3) Set the viscometer to scan between 10 and 1000 seconds<sup>-1</sup> and use a ramp up/ramp down protocol for viscosity measurement. Fifty measurements are made in the ramp up portion and fifty measurements in the ramp down portion.

#### Data Recording and Analysis

Record the viscosity from each of two samples at shear rates of 100 seconds<sup>-1</sup> and 1000 seconds<sup>-1</sup> shear rate from the ramp down portion of the protocol.

### Charge Density

#### Overview

Charge density of a dispersion or a colloidal solution can be measured by measuring the electrical potential (streaming potential) between a pair of spatially separated electrodes one of which is adjacent to a surface of a sample container where the particles of the dispersion or the macromolecules from a colloidal solution have been caused to adsorb and the other of which is positioned in the free volume of the sample container. The counterions for any charged particulate or macromolecular species are caused to flow by an oscillating piston setting up the electrical potential. The sample is then titrated to a zero streaming potential (i.e. to the isoelectric point) with a standard polyelectrolyte having the opposite charge to measure charge density in microequivalents per gram.

#### Apparatus

**Particle Charge Detector:** A suitable apparatus for measuring charge density is available from MÜTEK Analytic, Inc. of Marietta, GA as Particle Charge Detector PCD 02.

**Titration:** A suitable titration is the Mettler automatic endpoint titration model DL21 with two piston burettes which is also available from MÜTEK Analytic, Inc. of Marietta, GA

#### Standard Materials

Standard polyelectrolyte solutions are also available from MÜTEK Analytic. The cationic standard is 0.001N poly-diallyl-dimethyl-ammonium chloride. The anionic standard is 0.001N sodium polyethylene sulfate.

#### Operation

- 1) Set up and calibrate the particle charge detector according to the manufacturer's directions. Importantly, the ambient temperature should be greater than 15°C, preferably about 25°C, for accurate measurement.
- 2) Set up and calibrate the titration according to the manufacturer's instructions.

- 3) Rinse the sample cell and the piston of the particle charge detector with sample. The sample may be filtered (100 mesh strainer) to remove large particles which may interfere with operation of the piston although being only a small portion of the charged species.
- 4) Dispense a controlled amount of sample into the rinsed sample cell. A preliminary titration may be necessary to determine the amount of sample that will require between 0.5 and 15 milliliters of titrant. At least 10 milliliters of liquid is required to cover both electrodes. Samples may be diluted with deionized water to provide a sample of at least 10 milliliters volume that requires between 0.5 and 15 milliliters of titrant.
- 5) Insert the piston into the sample container and place the container into the particle charge detector, insuring that the electrodes are in contact and the piston is engaged with the drive mechanism.
- 6) Turn the piston on and allow the streaming potential to stabilize (about 2 minutes).
- 7) Titrate the sample to the isoelectric point using the appropriate polyelectrolyte solution. That is, titrate cationic samples with the anionic polyelectrolyte and titrate anionic samples with the cationic polyelectrolyte.

#### Data Recording and Analysis

- 1) Record the amount of titrant required to take the sample to the isoelectric point.
- 2) Calculate charge density  $q$  (microequivalents per gram) using the following equation:

$$q = \frac{V \times C \times 1000}{W}$$

Where:  $V$  is the volume of titrant required (milliliters);  $C$  is the polyelectrolyte concentration (microequivalents per milliliter); and  $W$  is the solids content in the sample (e.g. for a 10 milliliter sample of a 0.1%  $\text{TiO}_2$  suspension,  $W=0.01$  grams)

- 3) Report the result of each measurement made.

### Particle Size Distribution

#### Overview

The particle size distribution of the pigment particles formed in the process of the present invention may be measured using a light scattering apparatus. Both coherent and non-coherent light sources are used, depending on the expected range of particle sizes.

#### Apparatus

A suitable apparatus is available from Horiba Instruments, Inc. of Irvine, CA as Model LA910. The Horiba LA910 measures the Particle Size Distribution (PSD) using a scattering system. Both a coherent light source (laser) and a non coherent light source are provided for measurement of a wide range of PSDs. This apparatus can determine four distributions (Volume, Number, Area and Length) for a given sample. Software is provided for an attached computer to control the apparatus and to convert the light intensity data that is actually measured into any of the above-identified distributions. The Volume Distribution is preferred to follow structural changes. Median particle size is preferred as a single number descriptor of PSD so as to provide a proper description for cases which depart from a normal distribution. The Horiba LA910 has capability for low-power sonication (about 40 watts) to separate aggregates. Measuring the PSD without sonication is preferred to better understand any agglomeration that may result from a particular mixing process.

#### Standard Materials

Calibration Standard Nanosphere™ Standard Polystyrene particles as supplied by Duke Scientific of Palo Alto, CA. These standards are NIST traceable.

#### Apparatus Setup

Relative Refractive Index (RRI): 2.00-0.00i

Agitation: 3

Circulation: 4

Sonication: Off

### Method

- 1) Set up and calibrate the instrument according to the manufacturer's instructions.
- 2) Measure the particle size distribution for a blank (deaerated, deionized water) to check the instrument base line by filling the sample cell with the water and clicking on measure on the computer screen.
- 3) Place 150 milliliters of deaerated, deionized water into the sample cell and insert the cell into the apparatus.
- 4) Add the sample dropwise until the light transmission scale (blue scale) as measured by the apparatus is between about 70% and 75%.
- 5) Click measure on the computer screen to gather data from the sample and to determine the particle size distribution of the sample.

### Data Recording and Analysis

- 1) Measure particle size distribution for at least two samples.
- 2) Determine if the distribution is monodisperse or polydisperse.
- 3) For monodisperse distributions report the median particle size.
- 4) For polydisperse distributions report the particle size defined by each peak of the distribution.

### Turbidity

#### Overview

Turbidity is a measure of the opacity/cloudiness of liquid suspensions. Turbidity is measured by determining the amount of light scattering due to the suspended particles.

#### Instrument

Turbidimeter A suitable turbidimeter is available from HACH Company of Loveland, CO as Model 2100AN.

Standard Materials

Standard turbidity materials (StablCal Standards) having turbidity values of <0.1, 20, 200, 1000, 4000, and 7500 Nephelometric Turbidity Units (NTU) are also available from HACH Company.

Method

- 1) Set up and calibrate the turbidimeter according to the manufacturer's instructions.
- 2) Dilute 0.4 grams of the pigmented adhesive with 1000 milliliters of water and mix for one minute. A magnetic stirrer such as the Corning Model PC-351 as is available from Coning Glass Works (Corning, NY) is suitable.
- 3) Allow the diluted sample to equilibrate for 1 minute.
- 4) Transfer a suitable volume (~30 milliliters) to the sample cell.
- 5) Measure turbidity according to the manufacturer's instructions.
- 6) Record the measured turbidity.

Data Recording and Analysis

- 1) Report the turbidity value in Nephelometer Turbidity Units, NTU.

Mixing EnergyOverview

Current and voltage are measured and are used to calculate power delivered to the energizing means.

Instrument

**Power Analyzer** A suitable power analyzer is available from Fluke Corp. Of Everett, WA as a Model 41B Power Harmonics Analyzer.

**Amp Probe** A Model 80I-1000s, also available from Fluke Corp. is suitable.

Method

- 1) Insure power meter is calibrated according to manufacturer's instructions.

- 2) Place the amp probe around one of the three conductors of the electrical supply line for the energizing means. Attach voltage probes to the other two conductors of the supply line. The Fluke 41B calculates a three-phase power readout from a simple, single-phase measurement of a balanced three-conductor load. Power measurements were sent and recorded to a Microsoft Excel Spread Sheet using software supplied with the instrument (Fluke View version 3.0).
- 3) Measure power consumption with the tank empty by placing a small amount of water around the seal at the bottom. Measure the power consumption for the entire range of speed for the specific energizing means being evaluated.
- 4) Record the power reading from the power analyzer every 10 seconds at least 5 times through each addition step of the adhesive manufacture process described above. If desired, data acquisition hardware and software can be used to sample and record power readings automatically.

#### Data Recording and Analysis

- 1) Calculate Net Power for each addition step by subtracting the power consumption at the run speed from the power consumption while adding a material.
- 2) Calculate Net Power per Unit Mass for each step by dividing the Net Power by the mass of material being energized after the addition step.
- 3) Report Net Power and Net Power per Unit Mass for each addition step.



What is claimed is:

1. An adhesive composition for laminating an absorbent paper product, said adhesive composition comprising:  
from 2% to 7% by weight of a water-soluble or dispersible dry strength binder material;  
from 0.05% to 5% by weight of a water soluble, cationic wet strength resin;  
from 58% to 91% by weight water; and  
characterized in that said adhesive composition also comprises from 7% to 30% by weight of a pigment suspended in said adhesive composition.
2. An adhesive composition according to Claim 1 wherein said dry strength binder material is selected from the group consisting of polyvinyl alcohol, polyvinyl acetates, carboxymethyl cellulose resins, starch based resins, and mixtures thereof.
3. An adhesive composition according to any of the above claims wherein said pigment is selected from the group consisting of kaolin, calcium carbonate, zinc oxide, and titanium dioxide.
4. An adhesive composition according to any of the above claims wherein said pigment slurry is provided to said adhesive composition as a dispersion in water and said dispersion is stabilized using an anionic dispersion aid.
5. An adhesive composition according to any of the above claims wherein said water-soluble cationic resin is selected from the group consisting of polyamide-epichlorohydrin resins, gloxalated polyacrylamide resins, polyethyleneimine resins, and mixtures thereof.
6. An adhesive composition according to Claim 5 wherein said polyamide-epichlorohydrin resin comprises the reaction product of an epichlorohydrin and a polyamide containing secondary amine groups, the ratio of epichlorohydrin to secondary amine groups of said polyamide being from 0.5 to 1 to 2 to 1.

7. An absorbent paper product, said paper product comprising at least two plies of paper, wherein said plies are adhesively laminated using a laminating adhesive composition according to any of the above claims.
8. An absorbent paper product according to Claim 7 wherein said product comprises between 6 grams adhesive solids per kilogram of paper and 10 grams adhesive solids per kilogram of paper.
9. An absorbent paper product according to Claims 7 or 8 wherein said paper product is a paper towel.
10. A method for producing a pigmented adhesive composition, said method comprising the steps of:
  - a) providing an aqueous solution or dispersion of a first resin;
  - b) providing energizing means characterized in that said energizing means has a capability of transferring at least 5 watts per kilogram of power to said first resin solution or dispersion;
  - c) energizing said first resin solution or dispersion with said energizing means;
  - d) providing an aqueous dispersion of pigment particles, said pigment particles having a mean particle size;
  - e) mixing said pigment dispersion into said first resin solution or dispersion using said energizing means;
  - f) providing an aqueous solution or dispersion of a second resin; and
  - g) mixing said second aqueous resin solution or dispersion into said mixture of said first resin solution with said pigment dispersion using said energizing means to form said pigmented adhesive composition, wherein the median unsonicated particle size of said pigment particles in said pigmented adhesive composition is no larger than 2.5 times the median unsonicated particle size of said pigment particles in said pigment dispersion.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/09149

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 C09J201/02 D21H27/32

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09J D21H B32B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 018, no. 012 (C-1150), 11 January 1994 & JP 05 247889 A (OJI PAPER CO LTD), 24 September 1993 see abstract	1
A	WO 97 11226 A (PROCTER & GAMBLE) 27 March 1997 cited in the application see claim 1	1
A	WO 96 34149 A (PROCTER & GAMBLE) 31 October 1996 see claims 1,2	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/09149

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9711226 A	27-03-1997	AU 7104896 A EP 0848770 A	09-04-1997 24-06-1998
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